ELSEVIER

Journal of Alloys and Compounds 224 (1995) 203–206

Journal of
ALLOYS
AND COMPOUNDS

$Ag_6S_3O_4$ phase and its basic properties

Jadwiga Walczak [a], Flora Boccuzzi [b], Elżbieta Łukaszczyk-Tomaszewicz [a]

[a] *Department of Inorganic Chemistry, Technical University of Szczecin, Al. Piastów 42, 71-065 Szczecin, Poland*
[b] *Department of Inorganic Chemistry, University of Turin, Via P. Giuria 7, 10125 Turin, Italy*

Received 23 October 1994; in final form 10 January 1995

Abstract

Mixtures of Ag_2SO_4 and Ag_2S with a silver sulphate content varying from 16.67–50.0 mol.% were heated in air. The diffraction pattern of a sample obtained by the heating of a physical mixture comprising 33.33 mol.% of Ag_2SO_4 consists of diffraction lines that could not be attributed to any of the other phases existing in the Ag–O–S system. The lines have been ascribed to a new phase of monoclinic system having the formula, $Ag_6S_3O_4$, which has been ascertained by chemical analysis.

Keywords: Ag–O–S system; Silver sulphate; Silver sulphide

1. Introduction

Our studies on the mechanism and kinetics of the reaction taking place between Cu_2S and $CuSO_4$ in an atmosphere of sulphur dioxide showed that one of the intermediate products of the reaction was the phase having the formula Cu_2SO_2 [1–5]. The phase had not been known in the literature before. Special studies on its synthesis and properties showed the phase to be stable up to 328–332 °C, it being the temperature range at which the phase melted congruently [1–5]. Cu_2SO_2 was obtained in the solid state according to the total equation of the reaction:

$$2Cu_2S + 2CuSO_4 = 3Cu_2SO_2 + SO_2 \qquad (1)$$

However, the phase appeared to be unobtainable in a pure form [1–5].

In the light of the information collected it deemed advisable to ascertain whether silver, the other element of the copper group could form a similar compound.

A literature scan preceding our investigations had shown that there existed four compounds in the Ag–O–S system: Ag_2O, Ag_2S, Ag_2SO_3 and Ag_2SO_4 [6–12]. The structure and the properties of the compounds are well known [6–12].

Only one publication contained information that there existed in the system yet another phase, $Ag_8S_3SO_4$ ($Ag_8S_4O_4$) – analogous to $K_8S_3SO_4$ [13].

Our in-depth studies were aimed at identification of the Ag_2SO_2 phase in the presence of five other phases. These studies show that the reaction in air of an equimolar mixture of Ag_2S with Ag_2SO_4 led to a new phase assumed to have the formula Ag_2SO_2 [14]. Like Cu_2SO_2, Ag_2SO_2 could not be obtained in the pure state [14].

2. Experimental

The following reagents were used for the experiments: Ag_2SO_4 p.a. and pure Ag_2S (products of POCh Glivice, Poland). The reagents, weighed in appropriate molar proportions, were homogenized by long-term grinding and then heated in air for a few cycles. After each heating cycle the samples were cooled to ambient temperature, ground and analyzed by DTA and X-ray diffraction and afterwards heated again until equilibrium was established.

DTA was made in quartz crucibles, in air at the heating rate of 10 ° min^{-1}. The weight of each sample was 1000 mg.

X-ray diffraction of the samples obtained was performed using a diffractometer DRON-3 using CoKα radiation.

Chemical analysis of the samples was done after the last heating cycle. Silver was determined by titration of weighed amounts of the samples dissolved in HNO_3 with a standard solution of NH_4SCN. The total amount of sulphur was determined gravimetrically, the element having previously been oxidized with Br_2 to SO_4^{2-} and then precipitated with $BaSO_4$.

SSDI 0925-8388(95)01547-7

Table 1
Chemical analysis of the new phase after washing Ag_2SO_4 with water

Component	Results of determination (mass fraction) 1	2	3	average	Calculated component contents of $Ag_6S_3O_4$ (mass fraction)
Ag	80.17	80.17	80.17	80.17	80.16
S	11.46	11.55	11.79	11.60	11.91
O	–	–	–	8.23	7.93

Table 2
Results of indexing the diffraction pattern of $Ag_6S_3O_4$ phase

No.	d_{obs} (Å)	d_{cal} (Å)	$h\ k\ l$	I (%)
1	6.14	6.14	0 1 1	10
2	5.57	5.58	1 0 2	5
3	4.82	4.82	$\bar{1}$ 1 2	10
4	3.84	3.84	2 1 2	4
5	3.77	3.77	4 0 1	4
6	3.546	3.546	$\bar{4}$ 1 2	14
7	3.119	3.122	$\bar{5}$ 0 3	10
8	3.072	3.072	0 2 2	52
9	2.993	2.996	$\bar{3}$ 2 1	66
10	2.930	2.935	0 1 4	6
11	2.901	2.906	4 1 2	23
12	2.785	2.788	2 0 4	6
13	2.758	2.754	$\bar{4}$ 1 4	13
14	2.734	2.738	5 0 2	10
15	2.691	2.692	$\bar{6}$ 1 2	100
16	2.629	2.629	$\bar{3}$ 2 3	7
17	2.574	2.572	3 2 2	13
18	2.529	2.532	$\bar{7}$ 0 1	7
19	2.417	2.416	$\bar{1}$ 2 4	37
20	2.383	2.384	3 1 4	6
21	2.366	2.362	$\bar{3}$ 2 4	3
22	2.323	2.323	5 2 1	10
23	2.287	2.290	1 2 4	80
24	2.245	2.246	2 3 0	7
25	2.216	2.214	$\bar{1}$ 0 6	16
26	2.191	2.194	2 1 5	34
27	2.150	2.149	3 0 5	7
28	2.049	2.050	$\bar{7}$ 2 1	14
29	1.9956	1.9982	$\bar{6}$ 0 6	7
30	1.8973	1.8953	2 1 6	16
31	1.8771	1.8753	$\bar{9}$ 0 4	5
32	1.8639	1.8636	5 3 1	3
33	1.8353	1.8346	6 1 4	11

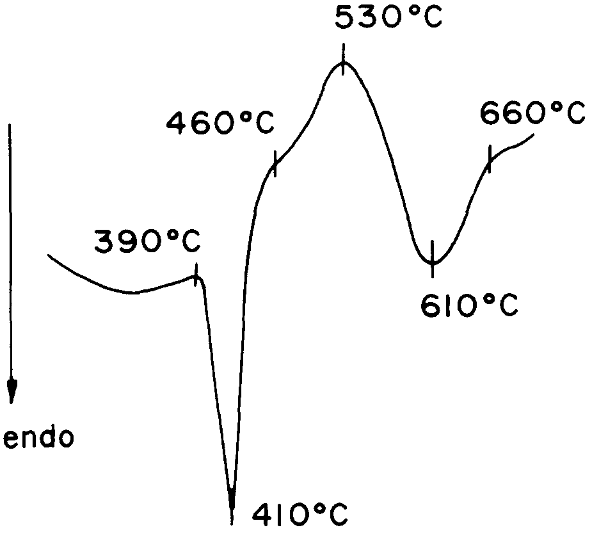

Fig. 1. DTA curve of $Ag_6S_3O_4$ phase for the temperature range 623–973 K.

3. Results and discussion

A hitherto unknown phase existing in the Ag–O–S system has been discovered through preliminary investigations. It has been found that the equimolar physical mixture of Ag_2S and Ag_2SO_4 melts at 390 °C without any mass change.

X-ray diffraction of the sample after cooling the melt to ambient temperature and grinding, led to a pattern containing a number of unidentifiable lines that could not be ascribed to any of the compounds existing in the Ag–O–S system. The reflections in the diffraction patterns were thought at first to be those of Ag_2SO_4 and the new phase. On the assumption that the following reaction was taking place between Ag_2S and Ag_2SO_4:

$$Ag_2S + Ag_2SO_4 = 2Ag_2SO_2 \tag{2}$$

the new phase was given a formula: Ag_2SO_2, as for the case of Cu_2SO_2.

However, further experiments showed that the reflections, previously attributed to Ag_2SO_4 and Ag_2SO_2, did not appear in samples rinsed with water. The afterwash residue was chemically analyzed to determine the content of silver and sulphur (the oxygen content was calculated from the difference).

The results are presented in Table 1, columns 1–5. Column 6 of the table shows the calculated percentage of $Ag_6S_3O_4$ ($Ag_6S_2SO_4$).

The data tabulated in Table 1 imply that a more likely formula for the new phase is $Ag_6S_3O_4$ rather than Ag_2SO_2.

In order to support this viewpoint, a number of physical mixtures of Ag_2S with Ag_2SO_4 were prepared, the contents of silver sulphate varying from 16.67–35.0 mol.%. The mixtures were heated in air at 360 °C for

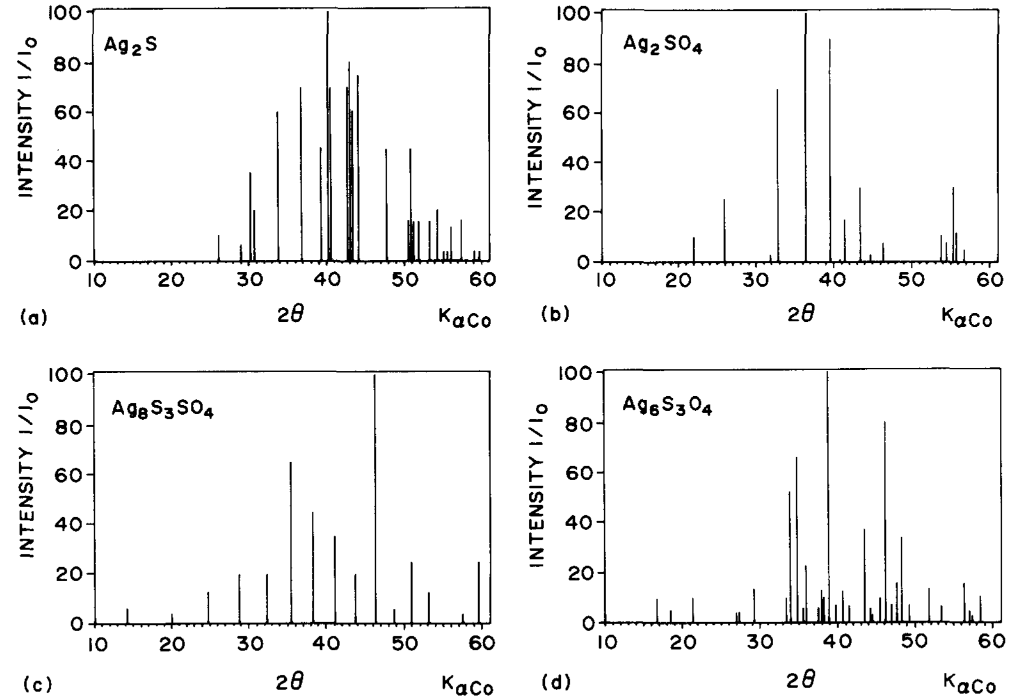

Fig. 2. Diffraction patterns within the 2θ 12–60°angle range for: (a) Ag_2S; (b) Ag_2SO_4; (c) $Ag_8S_3SO_4$; (d) $Ag_6S_3O_4$.

12 h and then 3 times at 290 °C for 48 h. It was only in the diffraction pattern of a sample comprising initially of 33.33 mol.% Ag_2SO_4 where any diffraction lines typical of the reagents or Ag_2SO_3 or $Ag_8S_3SO_4$ were present. The diffraction pattern contained only the diffraction lines which had previously been ascribed to the Ag_2SO_2 phase. These facts indicated that the new phase was formed by the following reaction:

$$2Ag_2S + Ag_2SO_4 = Ag_6S_3O_4 \qquad (3)$$

No diffraction lines characteristic of $Ag_8S_3SO_4$ have been found in the diffraction patterns of samples obtained by heating initial mixtures that contained 25 mol.% Ag_2SO_4 (compositions of the mixtures were corresponding with that of $Ag_8S_3SO_4$) [13].

$Ag_6S_3O_4$ phase is a brown–violet colour. Its density which has been measured by the method given in [15] is $\rho_{obs}(CCl_4) = 6.68 \pm 0.05$ g cm^{-3}.

Fig. 1 shows the DTA curve for $Ag_6S_3O_4$. The first endothermic effect recorded on the DTA curve has its onset at 390 ± 10 °C and may to be related with the congruent melting of $Ag_6S_3O_4$. The second endothermic effect with its onset at 530 ± 10 °C can be associated with the start of decomposition of liquid $Ag_6S_3O_4$. The fact is provable by the mass loss, recorded on the TG and DTG curves. The latter curves have not been included in the figure.

Fig. 2 shows the diffraction patterns of the reagents, $Ag_8S_3SO_4$ and that of the new phase, $Ag_6S_3O_4$ respectively.

The density of $Ag_6S_3O_4$ and the position of the diffraction lines at angle 2θ, determined by using an internal standard (α-SiO_2), were used to determine the crystal system and parameters of the unit cell. The determination was accomplished using an EDP program POWDER.

Table 2 shows the experimental values for the interplanar distances of $Ag_6S_3O_4$ and the values calculated by the computer application. The *hkl* indices and the relative intensities have been determined for each diffraction line. The lattice parameters are as follows: $a = 17.782 \pm 0.008$ Å; $b = 6.982 \pm 0.003$ Å; $c = 13.432 \pm 0.005$ Å; $\beta = 105.60 \pm 0.05°$. The volume of the unit cell is $V = 1606.22$ Å^3; the unit cell is of type P; the number of molecules in the unit cell $Z = 8$; the X-ray density $\rho_{rtg} = 6.68$ g cm^{-3}; $\Delta\rho(\rho_{rtg} - \rho_{obs}) = 0$.

The consistency of the values of the measured density and X-ray density, the relatively high value of the figures-of-merit for fitting all reflections, and the fact that indexing of all the observable diffraction lines at the considered angle range of 2θ 12 − 60° could be made, allow the ascertainment that the $Ag_6S_3O_4$ phase is a substance crystallizing in a monoclinic system and the unit cell can be characterized by the parameters quoted.

References

[1] H. Dębiński and J. Walczak, *J. Therm. Anal.*, *29* (1984) 971.
[2] H. Dębiński and J. Walczak, *J. Therm. Anal.*, *31* (1986) 779.
[3] H. Dębiński and J. Walczak, *J. Therm. Anal.*, *32* (1987) 35.
[4] H. Dębiński and J. Walczak, *Thermochim. Acta*, *117* (1987) 1.
[5] J. Walczak, H. Dębiński, B. Muraszko and P. Wiśniewski, *J. Therm. Anal.*, *34* (1988) 1257.

[6] *Joint Committee of Powder Diffraction File*: 4-774, 12-793, 14-72, 27-1403, 40-1471.

[7] R.C. Sharma and Y.A. Chang, *Bull. Alloy Phase Diagrams, 7* (1986) 267.

[8] A.J. Frueh, *Z. Kristallogr., 110* (1958) 136.

[9] L.S. Ramsdell, *Am. Miner., 28* (1943) 401.

[10] L.O. Larsson, *Acta Chem. Scand., 23* (1969) 2261.

[11] H.I. Berthold, I. Born and R. Wartchow, *Z. Kristallogr., 183* (1988) 309.

[12] N. Maschiocchi and W. Parrish, *Powder Diffraction, 5* (1990) 50.

[13] H. Hirsch, *J. Appl. Crystallogr., 12* (1979) 129.

[14] J. Walczak and E. Łukaszczyk, *6th Polish Sem. St. Bretsznajder, Płock, September, 1993*, University of Warsaw, 1993, p. 257.

[15] Z.Kluz and I.Wacławska, *Rocz. Chem., 49* (1975) 839.